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Very fine aerosols from the World Trade Center collapse piles: Anaerobic Incineration?

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By September 14, three days after the initial World Trade Center collapse, efforts at fire suppression and heavy rainfall had extinguished the immediate surface fires. From then until roughly mid-December, the collapse piles continuously emitted an acrid smoke and fume in the smoldering phase of the event. Knowledge of the sources, nature, and concentration of these aerosols is important for evaluation and alleviation of the health effects on workers and nearby residents. In this paper, we build on our earlier work to ascribe these aerosols to similar processes that occur in urban incinerators. The simultaneous presence of finely powdered (circa 5 μm) and highly basic (pH 11 to 12) cement dust and high levels of very fine (< 0.25 μm) sulfuric acid fumes helps explain observed health impacts. The unprecedented levels of several

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metals in the very fine mode can be tied to liberation of those metals that are both present in elevated concentrations in the debris and have depressed volatility temperatures caused by the presence of organic materials and chlorine.

Introduction

The collapse of the World Trade Center structures (South Tower, North Tower, and WTC 7) presented two very different types of air pollution events:

1. Initial fires and collapse-derived "dust storm"
2. Continuing emissions from the debris piles

Both cases shared the unusual aspect of a massive ground level source of particulate matter in a highly populated area with potential health impacts. EPA (Devlin, 2002) summarized 5 causal factors most likely to explain the statistically solid data connecting fine PM2.5 aerosols and human health.

1. Biological aerosols (bacteria, molds, viruses…)
2. acidic aerosols
3. very fine/ultra fine (< 0.1 μm) insoluble aerosols
4. fine transition metals
5. high temperature organics

We especially needed to ascertain if these potentially causal factors were present in the WTC plumes.

The presence of fuels, including diesel and electrical insulating oils and combustible materials in the WTC buildings, and lack of oxygen were two factors that allowed the fire to burn for over 3 months. In order to better understand these aerosols, a DELTA Group rotating DRUM impactor was shipped to New York and set up on the roof of the DOE Environmental Measurement Laboratory (EML) at 201 Varick Street, 45 m above ground level and roughly 1.5 km NNE of the World Trade Center site. The DRUM operated until Late December, after the last surface fires had been extinguished. (Cahill et al, 2004)

The samples were collected in 8 size modes from the inlet (circa 12 µm) to 5.0, 2.5, 1.15, 0,75, 0.56, 0.34, 0.26 to 0.09 µm aerodynamic diameter (Cahill et al, 1985; Raabe et al, 1989; Raabe 1997). Samples were analyzed by a suite of non-destructive spatially resolved beam based techniques (Bench et al, 2002; DQAP v. 9/02, 2002) for mass, hydrogen as an organic surrogate, elements from sodium to molybdenum and some heavy elements by synchrotron x-ray fluorescence (S-XRF), particle size by scanning electron microscopy. Time resolution ranges from 1 ½ hr to 3 hr depending on the size of the exciting beam.

The presence of the WTC plume at Varick Street depended on both source emission rate and meteorology, with both wind direction and plume lofting as the key parameters. In addition, the nature of the aerosols themselves, especially as they deviated in concentration, size, and composition from upwind and regional aerosols, also provided information identifying WTC impacts. We chose the 5 parameters that deviated generally by an order of magnitude from typical regional and urban values:

1. Very fine (0.26 > Dp > 0.09 µm) aerosol mass > 3.0 µg/m3, (> 10 x background), in 3 to 6 hr plumes.

18 such events, typically 3 to 6 hr in duration at Varick Street, were seen in the month of October. Then we applied the additional criteria:

	# events
2. HYSPLIT wind in SSW quadrant	14 + 1 calm
3. Very fine organics > 1.0 µg/m3,	16
4. 2.5 to 5 µm cement dust EF > 2.5	16
5. 2.5 to 5 µm sulfate > 0.3 µg/m3	15
6. Simultaneous ground based 3 hr hazes plumes at LaGuardia airport, Lv < 15 km	5 (+ 3 days Sept.)

5 events met all 6 criteria, 4 more met 5 of the 6 criteria, and these 9 events are labeled “highly probable events”. Three events met only one or two of the parameters, and these are labeled “non-WTC plumes” or uncertain sources, including a local power plant. Six of the events met 3 or 4 of the parameters, and these were labeled “probable WTC influence”. The analysis that follows uses only data from the 9 highly probable events.

On most days, the plumes lofted above NYC so that only those on or near the WTC site breathed these aerosols.

Table 6 shows very fine particle values for six of the highly probable events plus background, a non-WTC plume event, and comparison data from two highly impacted sites using the same size and plume behavior from earlier studies. (Cahill et al, 1992; Reid et a, 1994; Seinfeld et al, 2004).

Date	WTC impact?	Mass (μg/m^3)	Organics (μg/m^3)	SiO_2 (μg/m^3)	H_2SO_4 (μg/m^3)	V (ng/m^3)	Ni (ng/m^3)
Oct. 7	No	0.5	0.04	0.02	0.1	0.1	0.1
Oct. 3	Yes	50.6	9.3	1.4	17.1	115	22.7
Oct. 4	Yes	9.3	3.2	2.6	3.7	61	8.0
Oct. 5	Yes	4.7	1.5	0.9	1.9	3	1.3
Oct.12	Yes	8.2	3.0	2.9	2.2	24	7.1
Oct.15	Yes	4.8	1.6	1.3	1.1	3	17.3
Oct.24	Yes	3.8	1.0	0.2	1.6	5	6.7
Oct.29	No	2.4	1.2	0.07	0.9	2	1.6
Kuwait	-	na	na	0.6	5.5	na	5.0

Beijing	-	na	na	1.1	6.7	0.8	1.8

Table 6 Results of aerosol sampling at Varick Street, October, 2001, for very fine ($0.26 > D_p > 0.09$ μm) particles.

Coarse particles were similar to the initial collapse aerosols (cement, dry wall, glass, ...) (Lioy et al, 2003), but had chemicals and soot from the ongoing combustion (Natusch et al, 1974 a, b). The presence of unprecedented (vis. Beijing, Kuwait) levels of very fine (0.26 > Dp > 0.09 μm) particles by mass and number in narrow plumes was more typical of an industrial source. Upwind sources were a very minor contribution as shown by direct comparison with upwind aerosol sites and size distributions grossly different from typical; ambient aerosols (Leifer et al, this volume). Very fine particles near the WTC site in May, 2002, were generally < 10% of the October, 2001 plume impact days at Varick Street.

Interpretation

Figure 1 shows an example of typical crustal elements (silicon, calcium, iron, and aluminum) in the very fine ($0.26 > D_p > 0.09$ μm) mode from October 2 to October 30, 2001.

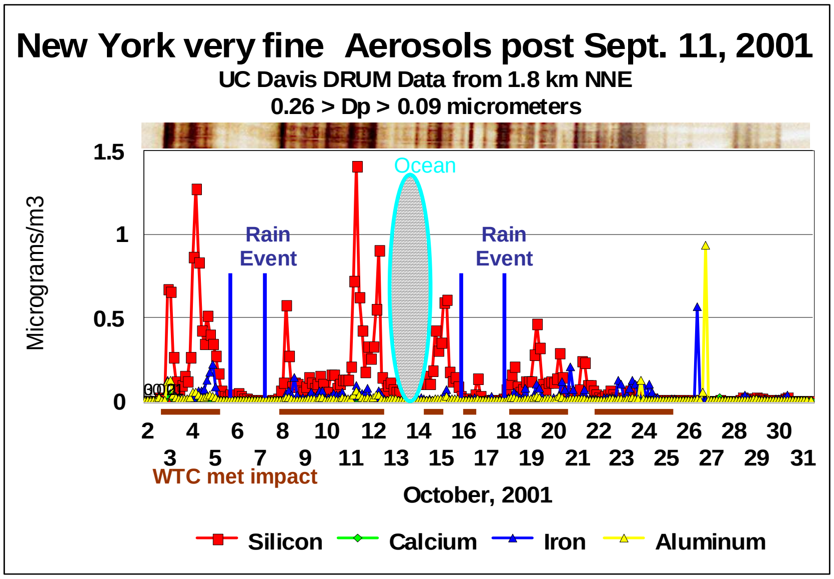


Figure 1 Typical crustal elements (silicon, calcium, iron, and aluminum) if the very fine particle ($0.26 > D_p > 0.09$ µm) mode from October 2 through October 30, 2001. On the top is shown the reflected light picture of this DRUM stage, and below the plot the meteorological favored wind direction that would bring the plume to Varick Street. Two rain events and an eastern ocean wind are also shown.

There are several important points to note in this figure, First, the other crustal elements (Al, Ca, and iron) seen so abundantly in the coarser particles are essentially absent in this very fine mode. Thus, the signal is not some sampling artifact, as is also shown by the low silicon values in the sub-micron sizes, and the mechanisms are not simply mechanical grinding. Second, the silicon only appears when the wind is correct. Third, the peak values trend downward in October, and even the color grows fainter. October 24 was by all accounts (meteorology, coarse calcium, ..) a very strong plume impact, but by then the silicon has gone. The same pattern is seen in some other anthropogenic elements, notably vanadium), in both the coarse and fine modes.

These data then pose problems of the aerosol sources. We see aerosols typical of a high temperature industrial source, yet the temperatures in the near sub-surface collapse piles were not very high. We see some elements vastly enhanced over typical Earth crystal values and others, equally present in the dust, absent in the aerosols. We propose a model derived from the theory and data on municipal incinerators. It was discovered that the presence of organic matter and especially chlorine in the wastes liberated metals by greatly reducing their volatility temperatures. (, Barton et al, 1990; Seeker at al, 1990, and references therein).

In Table 2, we present these data for EPA criterion metals and a few others of interest. The data are ordered by volatility temperature (the point at which the vapor pressure reaches 10^{-6} atmospheres).

Incineration with 10% chlorine	Boiling Point	Earth Crustal	Bulk Dust EPA	Bulk dust Lioy	Volatility Temp	Principal Species
Metal	^oC	ppm	ppm	ppm	^oC	
Chromium	2639	102	71.5	165	1594	CrO_2/O_3
Beryllium	1280	2.8	1.7	3.2	1042	$Be(OH)_2$
Barium	1634	425	195	381	895	$BaCl_2$
Nickel	2834	84	15.5	43.5	686	$NiCl_2$
Antimony	697	0.2	na	na	653	Sb_2O_3
Silver	2190	0.004	4.9	2.3	620	AgCl
Selenium	Na	0.05	< 1	na	315	SeO_2
Cadmium	761	0.15	3.8	7.2	211	Cd
Vanadium	3480	120	18.3	38.9	147	VCl_4
Thallium	1464	9.6	< 1	1.4	136	TlOH
Osmium	4224	0.0015	Na	na	40	OsO_4
Arsenic	814	1.8	< 1	2.6	32	As_2O_3

Mercury	353	0.085	0.37	nd	25	Hg
$Si0_2$	1725	9000	na	na	12	$SiCl_{414}$
Lead	1748	14	98	305	-12	$PbCl_4$

Table 2 Concentration in the WTC dusts and volatility temperatures of elements in the presence of 10% chlorine.

Note that the levels of many metals is greatly enhanced over Earth crustal levels, as to be expected in the wreckage of a highly computerized building. The top elements, chromium, beryllium, and barium, all have volatility temperatures that are probably higher than most parts of the collapse piles, since steel was not melted but was observed to glow red when pulled from the piles. Nickel, antimony, and silver are marginal, but all the rest have volatility temperatures well below the documented temperature of the collapse piles during October.

The mechanism proposed is then the formation of gasses in the oxygen-poor, chlorine rich collapse piles, emission through the rubble and conversion at or near the surface into oxidized forms and thus very fine particles.

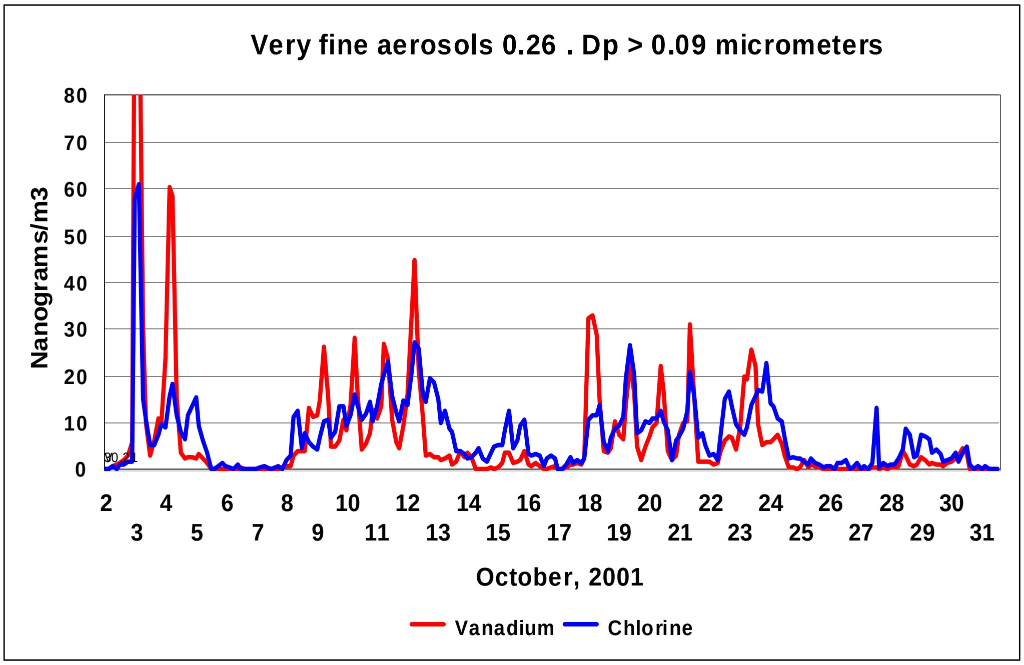
The other factor is concentration in the WTC dusts. The elements beryllium (which we can not analyze by S-XRF), antimony, silver, selenium, cadmium, thallium, osmium, arsenic and mercury are present only at the ppm levels in the WTC dusts, and thus would be unlikely in aerosols no matter what was the volatility temperature.

Combining these data into table 3, we see that the elements actually observed share the characteristics of relatively high concentrations in the collapse piles and low volatility temperatures. Other species, including most other crustal elements absent in the very fine mode, do not have depressed volatility temperatures are thus are not seen in the very fine aerosol.   Chromium and barium, both with high volatility temperatures, although abundant in the dusts, are largely absent in the aerosols. Vanadium and nickel are equally present in the dust, but because of the much lower vanadium volatility temperature, vanadium has 5 times more mass in the aerosols than nickel.

Very fine aerosols	October 7 background	October 3 WTC plume	Average abundance	Volatility temperature
0.26 – 0.09 μm	$\mu g/m^3$	$\mu g/m^3$	WTC dust	10% chlorine
Mass	0.53	50.7	na	na
Organics	0.04	9.3	na	na
Sulfur	0.04	5.6	na	na
	ng/m^3	ng/m^3	ppm	^oC
Silicon	11	698	abundant	12
Vanadium	0.1	114	30	147
Lead	< 0.5	26	200	-12
Nickel	0.1	23	30	686
Chromium	<0.1	1.5	120	1594
Barium	<0.1	<0.5	290	895

Table 3 Very fine aerosols versus concentration in dusts and volatility temperature.

Further evidence for the role of chlorine in releasing certain metals from the collapse piles is shown in Figure 2. Figure 2 shows vanadium and chlorine in the very fine mode aerosols but at ratio well below that of VCl_4.



Conclusions

By September 14, three days after the initial World Trade Center collapse, efforts at fire suppression and heavy rainfall had extinguished the immediate surface fires. From then until roughly mid-December, the collapse piles continuously emitted an acrid smoke and fume in the smoldering phase of the event. Knowledge of the sources, nature, and concentration of these aerosols is important for evaluation and alleviation of the health effects on workers and nearby residents. The simultaneous presence of very fine powdered and highly basic (pH 11 to 12) cement dust and high levels of very fine (< 0.25 µm) sulfuric acids fumes helps explain observed health impacts. The unprecedented levels of several metals in the very fine mode can be tied to liberation of those metals that are both present in the debris and have depressed volatility temperatures caused by the presence of organic materials and chlorine. These plumes have the potential for health impacts, as potentially causal factors health in very fine particles reached unprecedented ambient levels in the very fine aerosol plumes from the WTC collapse piles. This would effect workers at the site who did not use adequate repirators but because of plume lofting would not have affected most New York residents away from the site.

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